Thermochimica Acta 637 (2016) 120–131

Contents lists available at ScienceDirect

Thermochimica Acta

journal homepage: www.elsevier.com/locate/tca

Investigation on thermophysical properties of $RE_6UO_{12}(s)$ (RE = La, Pr, Nd, Sm)

Manjulata Sahu[a,*], K. Krishnan[b], Dheeraj Jain[c], M.K. Saxena[a], Smruti Dash[d]

[a] Radioanalytical Chemistry Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400085, India
[b] Fuel Chemistry Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400085, India
[c] Chemistry Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400085, India
[d] Product development Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400085, India

ARTICLE INFO

Article history:
Received 25 August 2015
Received in revised form 4 June 2016
Accepted 6 June 2016
Available online 7 June 2016

Keywords:
Combustion method
High temperature X-ray diffractometry (HT-XRD)
Differential scanning calorimetry (DSC)
Thermogravimetry (TG)
X-ray photoelectron spectroscopy (XPS)

ABSTRACT

$RE_6UO_{12}(s)$ (RE = La, Pr, Nd, Sm) was synthesized by citrate-nitrate combustion method. The synthesis condition for $Pr_6UO_{12}(s)$ was optimized. Nonstoichiometry in these rare earth uranates in argon atmosphere was analysed using various techniques like thermogravimetry (TG), X-ray photo electron spectroscopy (XPS), chemical analysis and electrical conductivity measurements. Thermal expansions of $RE_6UO_{12}(s)$ (RE = Pr and Sm) was studied in the temperature range 298–1273 K by high temperature X-ray powder diffractometry and compared with that of similar rare earth compounds reported in the literature. Heat capacity of $RE_6UO_{12}(s)$ (RE = La, Pr, Nd, Sm) was measured by differential scanning calorimetry in the temperature range 300–870 K. Enthalpy, entropy and Gibbs energy functions of these compounds were computed from the measured heat capacity data.

1. Introduction

The rare earth uranates (RE_6UO_{12}) are important in both front as well as back end of the nuclear fuel cycles. In the front end of fuel cycle, fission products (FP) are generated during the fission of fissile nuclide in UO_2 and $(UPu)O_2$ fuel and the generated solid FP can alter properties of the fuel during its residence in the reactor [1]. The ultimate fate of fission products depends on various parameters like temperature, oxygen potential and burn up. To ensure that the fuel can be subjected to the desired linear heat ratings without melting of the fuel pin, a large number of physico-chemical data of simulated fuel including various phases or the combination of data of individual phases are required for the reactor designer. The thermal expansion and thermal conductivity are important among them. If the thermal expansion coefficient of FP will be higher than that of fuel, it induces stress to the clad and leads to fuel pin failure. Thus, thermal expansion data plays a key role in designing reactor code. The thermal conductivity of a material can be derived from heat capacity, density and diffusivity, which necessitates the determination of the important quantity like heat capacity. The fission yield of earlier rare-earths is high, hence its interaction with the fuel matrix cannot be ruled out. The RE-U-O system is characterized with both solid solutions and presence of $RE_6UO_{12}(s)$ type of compound [2–4]. Solid solutions are important from the point of view of its applications as burnable absorber in oxide fuel [5–8]. UO_2–Gd_2O_3 fuel has already been used in boiling water reactor (BWR) and earlier rare earths oxides have also been proposed for it. As RE_6UO_{12} exists in RE_2O_3-UO_2-O_2 system, its $\Delta m(O_2)$ is required to predict its formation under normal or off normal operating condition of the reactor. In the back end of the fuel cycle, $RE_6AnO_{12}(s)$ (RE = Y and Yb) (An = actinide elements) have been studied [9,10] as a host matrix for immobilization of actinides, to find out an alternative forms to glass matrices, which can have the maximum loading of radionuclide in small volume with high chemical and radiation stability. In order to correlates various properties of *f*-block compounds, their thermodynamic properties need to be determined. Though some scattered data on physicochemical properties of $RE_6UO_{12}(s)$ are reported in the literature [11–18], but systematic investigation on the complete series $RE_6UO_{12}(s)$ (RE = La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu) have not been reported. Hence, systematic investigations on thermophysico chemical properties of $RE_6UO_{12}(s)$ have been initiated in author's laboratory, of which thermophysical properties of $RE_6UO_{12}(s)$ (RE = Gd, Tb, Dy) have already been reported [19,20]. This study is focused on synthesis and characterization of $RE_6UO_{12}(s)$ (RE = La, Pr, Nd, Sm).

* Corresponding author.
E-mail addresses: manju@barc.gov.in, manju.igcar@yahoo.com (M. Sahu).

http://dx.doi.org/10.1016/j.tca.2016.06.004
0040-6031/

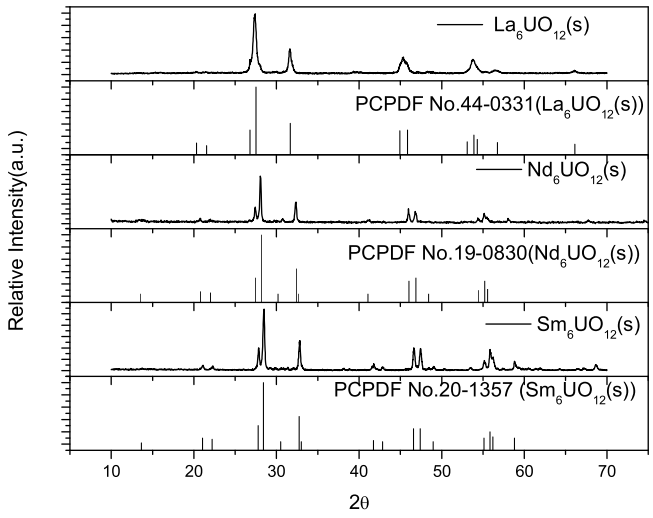

Fig. 1. XRD pattern of $RE_6UO_{12}(s)$ (RE = La, Nd and Sm) synthesized in air at 1473 K for 24 h.

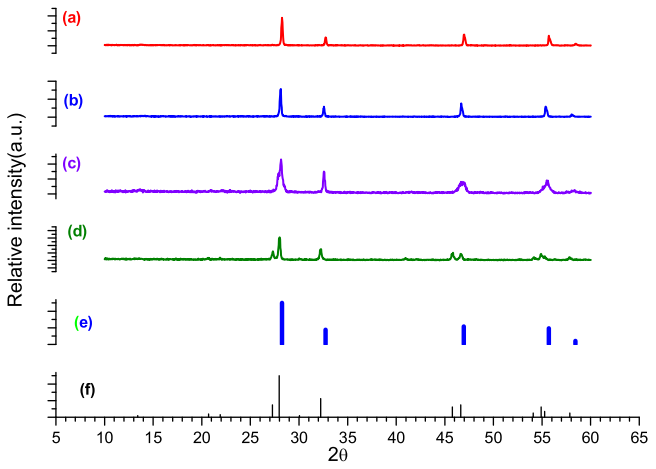

Fig. 2. Phase evolution of $Pr_6UO_{12}(s)$ (a) $Pr_6O_{11}(s)$ was heated at 1473 K for 24 h in oxygen(b) $Pr_6UO_{12}(s)$ was heated at 1273 K for 6 h and 1373 K for 6 h in air(c) $Pr_6UO_{12}(s)$ was heated at 1373 K for 8 h in argon(d) $Pr_6UO_{12}(s)$ was heated at 1473 K for 8 h in argon (e) the reported XRD pattern for cubic $UO_2(s)$(PCPDF No. 73–2293) (g) the reported XRD pattern for rhombohedral $Pr_6UO_{12}(s)$ (PCPDF No. 19–1020).

The synthesized and XRD identified rare earth uranates were analysed with techniques like thermo gravimetry, X-ray photo electron spectroscopy (XPS), chemical analysis and electrical conductivity to determine their stoichiometry. The thermal expansion coefficient of $RE_6UO_{12}(s)$ (RE = Pr and Sm) was determined using high temperature X-ray diffraction method in the temperature range 298–1273 K and heat capacity of $RE_6UO_{12}(s)$(RE = La, Pr, Nd, Sm) was measured by differential scanning calorimetry in the temperature range 300–870 K. Both the measured values were compared with the corresponding values for similar rare earth uranates available in the literature. Enthalpy increments, entropies and Gibbs energy functions of $RE_6UO_{12}(s)$ (RE = La, Pr, Nd, Sm) have been derived from the measured heat capacity values.

2. Experimental

2.1. Material preparation & characterisation

Citrate–nitrate gel combustion method was adopted for the synthesis of $RE_6UO_{12}(s)$ (RE = La, Pr, Nd, Sm). $U_3O_8(s)$ $La_2O_3(s)$, $Pr_6O_{11}(s)$, $Nd_2O_3(s)$ and $Sm_2O_3(s)$ were used as initial reactants. Citric acid, selectipure HNO_3 and NH_3 solution were also used in various steps of synthesis process. The sample table for all the chemicals being used in the various steps of synthesis is given in Table.1. The rare earth content in $La_2O_3(s)$, $Pr_6O_{11}(s)$, $Nd_2O_3(s)$ and $Sm_2O_3(s)$ solutions used for synthesis were determined using inductively coupled plasma mass spectrometry (ICPMS). The experimental procedure followed was similar as described in our earlier work [20]. $RE_6UO_{12}(s)$ (RE = La, Nd and Sm) was synthesized by heating the corresponding precursor in air at 1473 K for 24 h as La^{+3}, Nd^{+3} and Sm^{+3} are stable in air. However, Pr has variable oxidation states and Pr^{+3} is stable in low oxygen partial pressure. In order to verify it, praseodymium oxide received from Rare Earth Development Division, BARC, Mumbai was heated at 1473 K for 24 h in oxygen and its XRD pattern matched with $Pr_6O_{11}(s)$ (PCPDF No:42-1121), in which Pr exists in mixed valence states of +3 and +4 [21]. But Pr^{+3} is required for synthesis of $Pr_6UO_{12.}$ (s). To establish its synthesis conditions, initially the precursor of Pr $_6UO_{12}(s)$ was heated in air, which was subsequently heated in high purity argon atmosphere. The colour of the reaction product obtained from the precursors for $La_6UO_{12}(s)$, $Pr_6UO_{12}(s)$, $Nd_6UO_{12}(s)$, and $Sm_6UO_{12}(s)$ were intense yellow, greyish black, turmeric yellow and gentle yellow, respectively. Stoe theta–theta X-ray diffractometer with monochromatic Cu Kα radiation (kα = 0.15406 nm) was employed to confirm the synthesized phases. The scans were made in the range of $10^{\circ} \leq 2\theta \leq 60^{\circ}$. The XRD pattern obtained for $RE_6UO_{12}(s)$ (RE = La, Nd and Sm) is given in Fig. 1, whereas the XRD pattern evolved in various stages of synthesis of Pr_6UO_{12} is given in Fig. 2(a–f). The stoichiometry of $RE_6UO_{12}(s)$ (RE = La, Pr, Nd, Sm) were studied using various techniques like thermogravime-

Table 1
Sample Table of various chemicals being used in the synthesis of $RE_6UO_{12}(s)$(RE = La, Pr, Nd, Sm).

Chemical Name	Source	Initial Mole Fraction Purity	Final mole Fraction Purity	Analysis Method
Lanthanum(III)oxide, $La_2O_3(s)$	REDS, BARC[a]	0.9995		ICPAES[b]
Praseodymium(III,IV) oxide, $Pr_6O_{11}(s)$	REDS, BARC[a]	0.9995		ICPAES[b]
Neodymium(III) oxide, $Nd_2O_3(s)$	REDS, BARC[a]	0.9995		ICPAES[b]
Samarium(III) oxide, $Sm_2O_3(s)$	REDS, BARC[a]	0.9995		ICPAES[b]
Uranium(V,VI) oxide, $U_3O_8(s)$	Nuclear Fuel Complex, Hyderabad, India	0.9999		AES
3-carboxy-3-hydroxypentane-1,5-dioic acid	Chemco fine chemicals, Mumbai	0.997		Titration
Supra pure HNO_3	M/s Merck Ltd, Germany	0.9999		Titration
NH_3 solution	M/s Chemco fine chemicals, Mumbai	0.95		Titration
$La_6UO_{12}(s)$	Synthesis		0.997	ICPMS[c]
$Pr_6UO_{12}(s)$	Synthesis		0.992	ICPMS[c]
$Nd_6UO_{12}(s)$	Synthesis		0.987	ICPMS[c]
$Sm_6UO_{12}(s)$	Synthesis		0.995	ICPMS[c]

[a] Rare Earth Development section, BARC.
[b] Inductively coupled plasma atomic emission spectroscopy.
[c] Inductively coupled plasma mass spectroscopy.